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ROHM & HAAS COMPANY (10)
REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

TRAFLUOROHYDRAZINE

FC

(F_2N-NF_2)

A NEW HIGH ENERGY LIQUID OXIDIZER

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ROHM & HAAS COMPANY

REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

REPORT NO. S-22

TETRAFLUOROHYDRAZINE
(A new, high energy, liquid oxidizer)

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ABSTRACT

Tetrafluorohydrazine gives the following theoretical equilibrium impulses at 1000 psi → 1 atmos. with the following fuels:

H_2 - 357 sec.; N_2H_4 - 333; NH_3 - 325; UMDH - 316; Hidyne - 314; JP-4 -297.

The physical and chemical properties of tetrafluorohydrazine indicate that it would be much easier to handle as a liquid oxidizer than are oxygen and fluorine.

The preparation, chemical and physical properties of tetrafluorohydrazine are briefly reviewed.

TETRAFLUOROHYDRAZINE
(A new, high energy, liquid oxidizer)

The new heat of formation of tetrafluorohydrazine ($\Delta H^{c}_{f25}[N_2F_4]$ = -2.0 ± 2.5 kcal./mole)[1] which has been determined at the National Bureau of Standards indicates that tetrafluorohydrazine is a much more powerful oxidizer than previously believed. The calculated specific impulses (Table I) would indicate that tetrafluorohydrazine lies between fluorine and oxygen in its oxidative power. However, its physical and chemical properties are much superior to those of fluorine and oxygen (Table II).

It is immediately apparent from these tables that tetrafluorohydrazine exceeds liquid oxygen with all fuels listed (except hydrogen) and approaches the performance of fluorine as a high energy oxidizer. Because of its properties outlined in Table II it is much more readily handled than are fluorine and oxygen. Because of its low freezing point it would be easier to work with than is N_2O_4.

Preparation

The preparation of tetrafluorohydrazine was first reported by this Division[2]. Subsequent reports in this series have covered the development of satisfactory methods of preparation of tetrafluorohydrazine.

Tetrafluorohydrazine is prepared by the reaction at elevated temperatures of nitrogen trifluoride with various fluorine acceptors such as copper, arsenic, bismuth, antimony, glass[2,3] and carbon[4]. The

[1] G. T. Armstrong, S. Marantz and C. F. Coyle NBS Report No. 6584 October, 1959.
[2] Rohm & Haas Company Quarterly Progress Report on Physical Chemistry, No. P-57-4, March, 1957.
[3] C. B. Colburn, A. Kennedy JACS 80 5004 (1958).
[4] Stauffer Chemical Company Report No. SCC-26-QPR-6 December, 1958.

Table I

Specific Impulse[1] of Various Fuel Oxidizer Mixtures

Fuel		Oxidizer			
	N_2F_4	$N_2F_4^2$ N_2O_4	O_2	F_2	N_2O_4
Hydrogen	Eq.[3] 357		391[5]	410[5]	
	Froz.[4] 326		388[5]	398[5]	
Hydrazine	Eq. 333	—	313[5]	363[5]	292[5]
	Froz. 311		301[5]	334[5]	283[5]
Ammonia	Eq. 325		294[5]	357[5]	
	Froz. 306		285[5]	330[5]	
UDMH	Eq. 316		310[5]		285[5]
	Froz. 286		295[5]		274[5]
Hidyne[6]	Eq. 314		306[5]		282[5]
	Froz. 285		291[5]		271[5]
JP-4	Eq. 297	314	300[5,7]		276[5,7]
(CH_{1-93})	Froz. 277	285	286[5,7]		263[5,7]

[1] Calculated using ideal assumptions, expansion from 1000 psi to 1 atmos. See Rohm & Haas Company Quarterly Progress Report on Physical Chemistry, No. P-59-16, September 1959 for method of calculation.

[2] For carbon containing fuels it is interesting to note that a mixture of N_2F_4 and N_2O_4 will give a higher specific impulse than either constituent alone in much the same fashion as do mixtures of F_2 and O_2.

[3] Equilibrium flow.

[4] Frozen flow.

[5] These values taken from Rocketdyne Publication 505-X (Revised 1 January, 1959) "Rocket Engine Propellants".

[6] 60 wt. % UDMH 40% diethylene triamine.

[7] These numbers are for RP-1 which has essentially the same composition as JP-4.

Table II

Physical Properties of N_2F_4, F_2, O_2, N_2O_4

	N_2F_4	O_2[3]	F_2[3]	N_2O_4[3]
Boiling Point °C.	-73[1]	-183	-187	21.3
Melting Point °C.	-163 (approx.)	-218.4	-223	-9.3
Critical Temperature °C.	36[1]			
Critical Pressure Atmos.	77[1]			
Density gr/cc.	1.5[2] at -100°C.	1.14 $^{-183}$	1.108 $^{-187}$	1.491 ^{0}

[1] C. B. Colburn, A. Kennedy JACS 80 5004 (1958).
[2] Private communication Charles Mader to W. D. Niederhauser, 15 November, 1957.
[3] These values are handbook values.

reaction can be represented as follows:

$$2\,NF_3 + M \rightarrow N_2F_4 + 2\,MF$$

The loss of hydrogen by difluoroamine[1] on contact with various solids has also been reported to give tetrafluorohydrazine[2]. Electrical discharge through nitrogen trifluoride has also been reported as yielding tetrafluorohydrazine and difluorodiazine[3].

By far the most efficient method for the preparation of tetrafluorohydrazine is the reaction of nitrogen trifluoride with carbon[4]. This process has been perfected[5] and scaled up to a small pilot plant operation[6]. The yield of tetrafluorohydrazine from the reaction of nitrogen trifluoride with carbon is 77% at 440°C. with a residence time

[1] A. Kennedy, C. B. Colburn, JACS 81 2906 (1959).
[2] E. A. Lawton & J. Q. Weber JACS 81 4755 (1959).
[3] J. W. Frazer, I. Inorg. Z Nuclear Chem. 11 166-167 (1959).
[4] Stauffer Chemical Company Report No. SCC-26-QPR-6 December, 1958.
[5] Rohm & Haas Company Quarterly Progress Report on Physical Chemistry, No. P-59-9, June, 1959.
[6] Ibid., Quarterly Progress Report on Solid Propellant Processing, No. P-59-8 June, 1959.

of approximately six seconds. The yield is between 62-71% in the reaction between nitrogen trifluoride and copper at 375°C. and with a residence time of thirteen minutes. These reactions take place in flow systems and hence the process can be made continuous.

Summary of Chemical and Physical Properties of Tetrafluorohydrazine

Heat of formation	= -2.0 ± 2.5 kcal./mole
Boiling point	- 73°C.
Freezing point	-162°C. (approximately)
Critical temperature	36°C.
Critical pressure	77 atmospheres (estimated)
Vapor pressure equation	
$\log P_{(mm)}$	= -692/T + 6.33
Density	1.5 gm./cc.
Heat of vaporization	3170 cal./mole

Mass Cracking Pattern of N_2F_4

(Obtained on a Consolidated Model 620 Mass Spectrometer)

m/e	Ion	Pattern
52	NF_2^+	90.6%
33	NF^+	100.0%
28	N_2^+	7.7%
19	F^+	4.7%
14	$N^{\pm}$	8.5%

Sensitivity div./m 19.0

Instrument sensitivity 100 div./m for m/e 43 for n butane.

Infrared Spectrum of Tetrafluorohydrazine

(See Fig. 1 Rohm & Haas Company QPR Physical Chemistry Report, P-57-10, page 1).

N. M. R. Spectrum of Tetrafluorohydrazine

The F^{19} nuclear magnetic resonance spectrum of tetrafluorohydrazine consisted of a single broad unresolved band at a field of approximately 75 p. p. m. lower than that of the F^{19} nuclei of trifluoroacetic acid. Resolution of the expected triplet was not observed.

Tetrafluorohydrazine does not react with glass, stainless steel, or copper at room temperature.

Summary

Tetrafluorohydrazine is a powerful new oxidizing agent which lies between liquid oxygen and liquid fluorine in its performance behaviour with conventional fuels. Its physical and chemical properties indicate that it would be much easier to work with in liquid motors than fluorine and oxygen. Tetrafluorohydrazine can be prepared with relative ease.

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